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## OPTICAL RECORDING MEDIUM [Hikari kiroku baitai]

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#### Claims

- A type of optical recording medium characterized by the fact that it has a composite layer, with fine grains of metal or semiconductor dispersed in a metal oxide thin film, and a semiconductor layer, which contacts at least one surface of said composite layer, formed on a base plate.
- 2. The optical recording medium described in Claim 1, characterized by the fact that the fine grains of metal or semiconductor are fine grains of Sn, In, Sb, Pb, Al, Zn, Cu, Ag, Au, or Ge, or an alloy with said metals or semiconductor as the principal component.
- 3. The optical recording medium described in Claim 1, characterized by the fact that the metal oxide is at least one type selected from the oxides of Sn, In, Al, Zr and Zn.
- 4. The optical recording medium described in Claim 1, characterized by the fact that the semiconductor laver is a Ge layer.

### Detailed explanation of the invention

The present invention pertains to a type of recording medium, which performs optical information recording/reproduction by means of changes in the reflectivity or transmissivity generated by irradiating a laser beam or other energy rays to deform or remove the positions of the recording layer irradiated with the energy rays by means of melting or the like.

Properties required on the optical disk and other optical recording media include high recording sensitivity at the wavelength region of the laser beam used as the recording light source, high S/N ratio of the reproduction signal, high recording density, high storage stability, and low toxicity.

For the heat mode type recording media for which the recording layer is melted to form bits due to rise in temperature of the portions irradiated with a laser beam, in order to increase the recording sensitivity, it is necessary to have a high spectral absorptivity of the recording layer, low melting point. low specific heat, low thermoconductivity, and thin recording layer. In order to increase the S/N ratio of the reproduction signal, it is required that the bits have aligned shape and size, no disturbance in the periphery of the bits, and, when reflected light is used for reproduction, a large difference in the reflectivity between the recording portion and the blank portion, and, for a high recording density, a low thermoconductivity. In addition, in order to obtain a recording medium with high storage stability, it is required that the recording layer have high oxidation stability and high moisture resistance.

At present, the most appropriate recording medium for laser is the type prepared by forming tellurium or a tellurium-arsenic alloy or another tellurium alloy thin film as the recording layer on a glass or plastic base plate. Said tellurium or tellurium alloy thin film has a high light absorptivity in the visible light/near-IR light wavelength region, and it has low thermoconductivity and low melting point. Consequently, it has a high recording sensitivity. Also, it can easily realize aligned bit shape and size, and has an appropriate reflectivity in the visible light/IR light wavelength region. Consequently, it can realize reproduction signal with a high S/N ratio, and other excellent properties needed for the heat mode type laser recording media. However, tellurium thin film and tellurium-arsenic alloy thin films have low oxidation stability and high toxicity. This is undesired. In order to improve the oxidation stability, a scheme has been proposed in which selenium is added to tellurium or tellurium-arsenic alloy, or a tellurium low-oxide is used. However, at present, there is no satisfactory method. Also, there is still no effective scheme for coping with the toxicity.

In consideration of the toxicity, as a recording medium more favorable than the tellurium-based recording medium on a glass or plastic base plate, or on an aluminum or other reflective layer formed on said base plate, a layer prepared by forming a layer of dye or a dispersion of dye in a polymer is formed. However, usually, the dyes have absorption wavelength on the shorter side with respect to the red light, and there is no stable dye with high absorptivity in the wavelength range of 750-850 nm as the

oscillation wavelength region of semiconductor lasers to be used as the main types of the light source for recording in the future. Consequently, the dye base recording media using semiconductor lasers as the recording light source are inappropriate for practical applications.

The present inventors have performed extensive research with the purpose of developing a type of optical recording medium with low toxicity, high oxidation stability and high water resistance. As a result of said research, it has been found that for the structure composed of a composite layer having specific metal or semiconductor fine grains with high oxidation stability and high water resistance dispersed in a metal oxide thin film with high chemical stability, and a recording layer made of a prescribed type of semiconductor contacting at least one surface of said composite layer, it is possible to obtain an optical recording medium for which the sensitivity is high, the S/N ratio of the reproduction signal is extremely high, the stability is high, and the toxicity is low. As a result, the present invention was reached.

As the gist of the present invention, the present invention provides a type of optical recording medium characterized by the fact that it has a composite layer, with fine grains of metal or semiconductor dispersed in a metal oxide thin film, and a semiconductor layer, which contacts at least one surface of said composite layer, formed on a base plate.

Figure 1 is a diagram illustrating an example of the layer constitution of the optical recording medium of the present invention. As shown in Figure 1, a composite layer prepared by dispersing metal or semiconductor fine grains in a metal oxide (hereinafter to be referred to as composite layer) is set on a base plate, and a semiconductor layer is formed on the surface of the composite layer. The energy rays incident from the base plate side or from the side opposite the base plate of the optical recording medium are absorbed by the semiconductor layer and composite layer, and the generated heat melts the composite layer, so that the melted portion of the composite layer together with the portion of the

semiconductor layer contacting it moves, and the bit formed in this case has changed optical properties, such as reflectivity, transmissivity, etc. when energy rays are irradiated on this portion of the medium.

This change in the optical properties is used for performing recording/reproduction.

Examples of the metal or semiconductor for use in the composite layer of the optical recording medium include Sn, In, Pb, Al, Zn, Cu, Ag, Au, Sb, Bi, Se, Te, and Ge, and alloys with said metals or semiconductor as the principal component. From the viewpoint of low toxicity, the preferred examples of metals and semiconductors include Sn, In, Sb, Pb, Al, Zn, Cu, Ag, Au, and Ge, and alloys mainly made of them. Said metals and semiconductors are characterized by the fact that in the oscillation wavelength region of the semiconductor laser, reflectivity is high, melting point is low, toxicity is low, and stability in air is high. Consequently, when said metals or alloys mainly made of them are used, the aforementioned characteristic features are lost. Caution should be taken with this.

The metal oxide for use in the composite layer of the optical recording medium of the present invention should have excellent chemical stability and low thermoconductivity. Here, the preferable examples include the oxides of Sn, In, Al, Zr and Zn. Especially when an oxide of Sn or In is used, it is possible to obtain a recording medium with excellent stability in air, high sensitivity, and high S/N ratio of the reproduction signal. Examples of the oxides of Sn and In include SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2-x1</sub>, In<sub>2</sub>O<sub>3-x3</sub>, and other low oxides, Sn<sub>2-y</sub>M<sub>3</sub>O<sub>2</sub>, In<sub>2-x</sub>N<sub>x</sub>O<sub>3</sub> and other types prepared by doping different types of metals in SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>. Here, x and z represent positive numbers of 0.5 or smaller; y represents a positive number of 0.25 or smaller; M represents Sb or In; and N represents Sn, Ge, Pb, Zn or another metal.

The filling rate of metal or semiconductor in said composite layer should be in the range of 0.3-0.95. If the filling rate is lower than 0.3, the absorptivity of the composite layer falls, and the temperature for melting the composite layer to a fluid state rises, so the recording sensitivity of the obtained optical recording medium decreases. When the filling rate rises above 0.95, the metal or semiconductor grains

dispersed in the composite layer start contacting each other, so that the grain size of the metal or semiconductor grains becomes larger, and thus the sizes and shapes of the recording bits become misaligned, the S/N ratio of the reproduction signal falls, and the thermoconductivity of the composite layer rises. As a result, the recording sensitivity falls.

For each layer of the composite layer in the optical recording medium of the present invention, the thickness should be in the range of 10-500 Å. If each layer of the composite layer is less than 10 Å thick, due to melting and flowing of the energy ray irradiated portion of the composite layer, formation of bits of the semiconductor layer can hardly take place, and the recording sensitivity of the recording medium falls. On the other hand, when each layer of the composite layer is over 500 Å thick, the energy needed for melting the energy ray irradiated portion of the composite layer to fluidic state becomes higher, so that the recording sensitivity of the recording medium falls. Especially when the thickness of each layer of the composite layer is in the range of 30-300 Å, it is possible to obtain a recording medium with high sensitivity and high S/N ratio of the reproduction signal.

Examples of the semiconductor layers for use in the optical recording medium of the present invention include Ge, Si, Se and other element semiconductors as well as AlSb, GaAs GaSb, InP, InAs, InSb, and other compound semiconductors. Especially when Ge is used as the semiconductor, it is possible to obtain a homogeneous layer with a high light absorptivity in the wavelength range of 750-850 nm. Consequently, it is possible to obtain a recording medium with a high sensitivity and a high S/N ratio of the reproduction signal. Even when the Ge layer is a thin film, it still has excellent oxidation stability and moisture resistance, as well as low toxicity. Consequently, it can be preferably used as a semiconductor layer in the optical recording medium of the present invention. In addition, a semiconductor layer as a thin film prepared by doping Ga, In, Sb or the like in Ge may also be used in the optical recording medium of the present invention.

The thickness of each layer of the semiconductor layer in the optical recording medium should be in the range of 10-200 Å. If each layer of the semiconductor layer is less than 10 Å thick, the obtained recording medium has low reflectivity and absorptivity of light in the wavelength range of 750-850 nm, the contrast between the recording portion and the blank portion cannot be high, and the S/N ratio of the reproduction signal becomes lower. When the thickness of each layer of the semiconductor layer is over 200 Å, even when the energy ray irradiation portion of the composite layer is melted to fluidic state, it is hard to form the bits of the semiconductor layer, so that the recording sensitivity of the recording medium falls. Especially, when the thickness of each layer of the semiconductor layer is in the range of 20-100 Å, it is possible to obtain a recording medium with a high S/N ratio.

As an embodiment of the optical recording medium of the present invention, a composite layer is formed on a base plate, and a semiconductor layer is then formed on said composite layer. Examples of the materials for the base plate include the sheets and films made of various types of thermoplastic and thermosetting resins, such as polymethyl methacrylate, polystyrene, polyvinyl chloride, polycarbonate, polyethylene terephthalate, polybutylene terephthalate, polyamide, epoxy resin, diallyl phthalate polymer, diethylene glycol bis-allyl carbonate polymer, polyphenylene sulfide, polyphenylene oxide, polyimide, etc. Especially, when the optical recording medium of the present invention is used as an optical disk of the form with reproduction light irradiated through the base plate, the base plate should be made of methyl methacrylate base polymer, styrene base polymer, polyvinyl chloride, polycarbonate, diethylene glycol bis-allyl carbonate polymer, epoxy resin, and other transparent plastic sheets. Also, when glass sheet, aluminum sheet or other metal sheet is used as the base plate, by forming composite layer and semiconductor layer as recording layer after formation of polymer layer on said base plate, it is possible to obtain a optical recording medium with a high sensitivity. Examples of said polymers include polystyrene, polymethyl methacrylate, polyisobutyl methacrylate, etc.

Figures 2-5 illustrate examples of the layer constitution of the optical recording medium of the present invention. In the following, an explanation will be given regarding the manufacturing method of the recording medium of the present invention with reference to the layer constitution.

The recording medium shown in Figure 2 is prepared as follows: after semiconductor layer (2) is formed on base plate (3), composite layer (1) is formed on said semiconductor layer (2). Then, said operation is performed repeatedly, with the semiconductor layer formed as the outermost layer. As a result, the semiconductor layer is formed as an n-layer laminate, and the composite layer is formed as an (n - 1)-layer laminate (here, n is a positive integer). The semiconductor layer and composite layer may be formed using various methods, such as vacuum vapor deposition method, ionization vapor deposition method, ion plating method, sputtering method, cluster ion beam method, etc. When the composite layer is formed, metal and semiconductor metal oxide are loaded in different crucibles, respectively, and they are simultaneously evaporated for vapor deposition in a vacuum of 1 x 10<sup>-3</sup> mm Hg or better. In said vacuum vapor deposition operation, one may adopt the following schemes: ionization vapor deposition method in which the evaporated particles are jonized, and they hit the surface of the semiconductor layer, or ion plating method in which while ionization is performed, a DC voltage is applied on the base plate side to accelerate the ionized particles. Also, the composite layer may be formed by setting both metal or metal oxide target and metal oxide target to perform simultaneous sputtering. In any of the aforementioned methods, when the composite layer is formed, near each evaporating source and target, a quartz film thickness sensor or other sensor head is set to detect the evaporating rate and the sputtering rate of the metal or semiconductor and the metal oxide, respectively, for control so that it is possible to obtain the composite layer with the prescribed filling rate of the metal or semiconductor and thickness.

The recording medium shown in Figure 3 can be prepared by forming composite layer (1) on base plate (3), then forming semiconductor layer (2) on said composite layer (1), and then repeating said

operations to laminate n composite layers and n semiconductor layers, respectively. The recording medium with the constitution shown in Figure 4 can be prepared by performing the same operation as that in manufacturing the recording medium with the constitution shown in Figure 2 so as to laminate n semiconductor layers (2) and n composite layers (1) on base plate (3). The recording medium shown in Figure 5 is prepared by laminating n composite layers (1) and (n - 1) semiconductor layers (2) on base plate (3) by performing the same operation as that in manufacturing the recording medium with constitution shown in Figure 3.

For the optical recording media of the present invention with constitution shown in Figures 2-5, it is preferred that the thickness of the recording layer (the overall thickness of the entire laminated composite layers and semiconductor layers) be in the range of 50-2000 Å. When the thickness of the recording layer is over 2000 Å, the volume of the energy ray irradiation portion of the recording layer becomes larger, so that when the energy rays are irradiated, the density of the absorbed energy falls. Consequently, the recording sensitivity of the recording medium falls, the shape of the periphery of each bit formed in this case tends to become disturbed, and the S/N ratio of the reproduction signal is adverse influenced. If the recording layer is less than 50 Å thick, the obtained recording medium has a small difference in the reflectivity and absorptivity of light between the recording portion and the blank portion, the contrast between the recording portion and the blank portion falls, and the S/N ratio of the reproduction signal cannot be increased. When the optical recording medium of the present invention is used in a reflection type optical disk, the preferable thickness range of the recording layer is 70-500 Å.

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For the optical recording medium of the present invention with the constitution shown in Figures 2-5, when the thickness of each layer of the composite layer is in the range of 10-500 Å, the thickness of [each layer of the] semiconductor layer is in the range of 10-200 Å, and the thickness of the recording layer made of a laminate of said composite layer and semiconductor layer is in the range of 50-2000 Å.

the value of n may be any integer of 1 or larger. Especially, when Ge is used as the semiconductor layer, and n is 2 or larger in the constitution shown in Figure 2, it is possible to obtain an optical recording medium with especially high stability and moisture resistance in air.

The recording layer in the optical recording medium of the present invention is highly stable the conventional environment, and there is no need to set a protective layer specifically. However, in order to protect it from mechanical impact and to prevent troubles in recording/reproduction caused by attachment of dust, etc., it is possible to set a protective layer on the recording layer. The protective layer may be made of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, or other inorganic material and organic polymer material.

For the optical recording medium of the present invention shown in Figures 2-5, when base plate (3) is transparent, the recording/reproduction light beam may be incident either from above or from below as shown in the figure.

The optical recording medium of the present invention has the following characteristic features: low toxicity, high sensitivity, high stability and high moisture resistance in air, and extremely high S/N ratio of the reproduction signal. Although the reason for said characteristic features of the optical recording medium of the present invention are not yet clarified at this time, it is believed that the reason is as follows. For the optical recording medium of the present invention, the recording layer is made of laminated film consisting of a composite layer and a semiconductor layer with different optical constants. Consequently, compared to the case when the recording layer is made only of a composite layer or semiconductor layer, the absorptivity and reflectivity of the energy rays are much higher even when the recording layer is very thin. As a result, the energy density is high at the portion of the recording layer irradiated with the energy rays, so that the recording sensitivity rises. At the same time, the contrast between the recording portion and the blank portion is high, so that the S/N ratio in reproduction rises. In addition, as the composite layer forming the recording layer is composed of a

metal oxide and fine grains of metal or semiconductor with grain size smaller than the wavelength of the light and dispersed in said oxide, compared to the bulk metal or semiconductor, it can be easier to form the fluid state in company with the adjacent semiconductor layer at a lower temperature. The fluidized portion of the recording layer has a higher surface energy than that of the melt of the metal or semiconductor alone, so there is a difference in the surface energy between the fluidized recording layer and the surface of the base plate in contact with it. As a result, movement of the fluidized recording layer becomes smooth, and bits can be formed more easily. It is believed that movement of the fluidized recording layer is caused by the difference in the surface energy between the fluidized portion and the solid phase surrounding it (see: Japanese Kokai Patent Application No. Sho 55[1980]-132536). For the optical recording medium of the present invention, the semiconductor layer can easily become an amorphous or microcrystalline structure, and the metal or semiconductor grains in the composite layer are very small. Consequently, it is believed that they have a major influence on the size and shape of the bits. Also, there is no influence of the crystal grain boundary caused by large crystals often observed in the conventional metal thin films. As a result, it is believed that under a low irradiating energy, it is possible to form bits with aligned shape and size and with little disturbance in the peripheral portion.

In addition, the semiconductor layer forming the recording layer in the optical recording medium of the present invention has a low thermoconductivity, and the metal or semiconductor fine grains are isolated from each other in the composite layer, so that the thermoconductivity of the composite layer also becomes lower. Consequently, the sensitivity of the recording medium rises. Also, by selecting an appropriate filling rate for the metal in the composite layer and appropriate thicknesses of the semiconductor layer and composite layer, it is possible to obtain a recording medium with the optimum spectral absorptivity and spectral reflectivity.

The metal or semiconductor and metal oxide for use in forming the recording layer of the optical recording medium of the present invention all have high stability in air and water, and low toxicity.

Consequently, the optical recording medium has excellent storage stability with low toxicity.

The optical recording medium of the present invention can be used not only as an optical disk for recording/reproduction of image files, document files, data files, and as computer external memory, but also as tape, card, microfiche, etc. that allow direct write/read by laser beam.

In the following, an explanation will be given in more detail regarding application examples of the present invention. However, the present invention is not limited to them.

In the following application examples, the filling rate refers to the proportion of the volume of the metal or semiconductor fine grains in the composite layer.

#### Application Example 1

A disk-shaped base plate made of polymethyl methacrylate and measuring 1.2 mm in thickness, 300 mm in outer diameter, and 35 mm in inner diameter, was fixed in a chamber of a vacuum vapor deposition device. In three crucibles, Ge (product of Fruuchi Kagaku K.K.,  $30 \otimes x 10$  mm t, purity of 99.999%), Sn (product of Fruuchi Kagaku K.K.,  $30 \otimes x 10$  mm t, purity of 99.999%), and SnO<sub>2</sub> (product of Fruuchi Kagaku K.K.,  $18 \otimes x 5$  mm t, purity of 99.99%) were loaded, respectively. While said base plate was driven to rotate at 20 rpm, with a vacuum degree of  $1 \times 10^{-6}$  mm Hg, the electron beam vapor deposition method was adopted to vapor deposit a Ge layer with thickness of 30 Å first; then, Sn and SnO<sub>2</sub> were irradiated with separate electron guns, respectively, to perform vapor deposition of Sn and SnO<sub>2</sub> while their evaporating rates were controlled. As a result, on the Ge layer, a composite layer of Sn and SnO<sub>2</sub> with filling rate of Sn of 0.8 and film thickness of 60 Å was formed. Then, by repeating said operation, on the composite layer of Sn and SnO<sub>2</sub>, a Ge layer with thickness of 20 Å, a composite

layer of Sn and  $SnO_2$  with thickness of 60 Å, and a Ge layer with thickness of 30 Å were sequentially laminated, forming a disk-shaped optical recording medium having a recording layer with thickness of 200 Å and having a constitution with n=3 as shown in Figure 2.

The obtained disk-shaped optical recording medium was used in recording test. In this case, the optical recording medium was driven to rotate at a velocity of 1800 rpm, while the oscillation light of a semiconductor laser (product of Hitachi, Ltd., HLP-1600, oscillation wavelength of 830 nm) modulated with a pulse width of 100 nsee at a repeating frequency of 5 MHz was irradiated on the recording layer after it passed through a collimating lens, condensing lens and the base plate to be focused to a beam diameter of 1 µm. It was found that the intensity of the laser beam on the recording surface of the disk needed to form a bit with minor diameter of about 1 µm is 6 mW. Also, reproduction was performed using a 1-mW laser beam for a recording signal. Under the conditions of a reference signal of 5 MHz and bandwidth of 100 kHz, the CN ratio measured by a spectrum analyzer was found to be 56 dB.

After recording under the aforementioned conditions, the recorded disk-shaped recording medium was loaded in a thermostatically controlled constant-temperature constant-humidity (60°C, 95% RH) vessel to perform moisture resistance and heat reference test for 120 days. No variation in the CN ratio was observed.

#### Comparative Example 1

Three disk-shaped base plates made of polymethyl methacrylate of the same type as that used in Application Example 1 were prepared, and, just as in Application Example 1, Sn and SnO<sub>2</sub> were co-vapor deposited on each base plate with their evaporating rates controlled, with rotational velocity of the base plate of 20 rpm and vacuum degree of  $1 \times 10^{-6}$  mm Hg, using the electron beam vapor deposition method, forming three types of samples each having only a composite layer with fine grains

of Sn dispersed in SnO<sub>2</sub> with filling rate of Sn of 0.8 and with film thicknesses of 100 Å, 180 Å and 300 Å, respectively.

For the three types of samples obtained, the same method as that adopted in Application Example 1 was used to perform recording/reproduction, with results listed in Table 1.

物介照照集 (人)	レーダ充強度 () (*V)	CNH (dB)
100	1 0	4 2
3 8 0	1 3	4 5
300	12.FC & 22 & 2 & 2	

1) 関係が「\*\*\* あのピットを形成させるのに必要な、タメスタ架とにおけるレーダを改立

Table 1.

- Key: 1 Film thickness of composite layer (Å)
  - 2 Laser beam intensity 1) (mW)
  - 3 CN ratio (dB)
  - 4 Recording cannot be performed at 12 mW
  - 5 1) The laser beam intensity on the disk surface needed for forming a bit with minor diameter of 1 um.

### Comparative Example 2

Two disk-shaped base plates made of polymethyl methacrylate of the same type as that used in Application Example 1 were prepared, and, just as in Application Example 1, Ge was vapor deposited on each base plate, with rotational velocity of the base plate of 20 rpm and vacuum degree of  $1 \times 10^6$  mm Hg, using the electron beam vapor deposition method, forming two types of samples each having only a Ge layer as recording layer, with Ge film thicknesses of 80 Å and 300 Å, respectively. For the two types of samples obtained, the recording test was performed under the same conditions as in Application Example 1. However, it was found that for both samples, no bit could be formed with a laser beam intensity of 12 mW, and recording failed.

As can be seen from Application Example 1 and Comparative Examples 1 and 2, compared to the optical recording medium of the present invention shown in Application Example 1, the samples prepared in Comparative Example 1 with only a composite thin film of Sn and SnO<sub>2</sub> has lower sensitivity and CN ratio. On the other hand, the sample prepared in Comparative Example 2 with only a Ge thin film as the recording layer has much lower sensitivity than the optical recording medium of the present invention.

#### Application Example 2

13 types of optical recording media, shown as sample Nos. 2-1 to 2-13 in Table 2, were manufactured by forming a recording layer on each of the disk-shaped base plates made of polymethyl methacrylate using the same method as in Application Example 1, using the metals and metal oxides listed in Table 2 to form composite layers with film thickness listed in Table 2 and semiconductor layers of Ge with film thickness also listed in Table 2 to form a laminated structure listed in Table 2 as the recording layer.

For the 13 types of disk-shaped optical recording media obtained, the same method as that used in Application Example 1 was adopted to measure the recording sensitivity and CN ratio, with results listed in Table 2. It was found that the moisture resistance is especially excellent when n is 2 or larger.

	19		b #	1	7-47 (A.M	E	Ð	23	248	Æ 49 H
KIIBS	SET CO	eunnu	CMICUS GHOERF	72. 5 1) (A)	77. 5 D (A)	Burg	2	W. 3 (A)	レーザ契約度 (水)	GNIL (di)
2-1	\$ n	SnOt	0.8	140	50	wan	1	190	7	5 3
2-2	0.1	ing Op	0.6	120	5.0	87 4 YE	Z	340	10	5 4
2 ~ 3	In	SnDe	0.8	70	3.0	# 5 B3	3	270	Ţ	5.0
2-4	Sn	A 1 2 O 2	0.9	150	5.0	#3 2 EJ	2	250	12	4 9
2-5	10	2.0.	0.9	70	3.0	14 E	4	330	12	5.0
3 - 6	Sn	200	0.8	60	20	RI	3	2 6 0	11	50
2 - 7	G e	S n O e	3,8	8.0	4.0	16.2 Ed	3	280	8	5 5
2 - 8	Pb	In; Qa	9.8	140	5.0	田下	2	2 4 0	7	3.2
2-9	A 1	SnO2	0.7	80	20	FI LE	+ 4	260	10	5.0
\$ -10	ž o	SnOz	0.8	10	30	1, 19	3	130	10	5.0
2-11	Cu	SnOz	0.7	60	2 0	四 .b	- (	260	12	5.3
2-12	Αe	SnOz	0.7	6.0	.20	Ø .E	4	200	10	5.5
2-13	Λu	Ing Op	0.7	6.0	20	印止	Ł	260	12	5.5
2-14	S b	S n O;	0.9	100	10	日上	1	270	6	57

1) 12 4 2 - 3 0 2 8

2) # # 15 H - H 0 17 3

Table 2.

# Key: 1 Sample No.

- 2 Composite layer
- 3 Semiconductor layer
- 4 Recording layer
- 5 Recording/reproduction characteristics
- 6 Metal or semiconductor
- 7 Metal oxide
- 8 Filling rate of metal or semiconductor
- 9 Thickness 1) (Å)
- 10 Thickness 2) (Å)
- 11 Layer configuration

- 2 n
- 13 Thickness (Å)
- 14 Laser beam intensity (mW)
- 15 CN ratio (dB)
- 16 1) Thickness of each layer of the composite layer
- 17 2) Thickness of each layer of the semiconductor layer

#### Application Example 3

A disk-shaped base plate made of diethylene glycol bis-allyl carbonate polymer (commercial name CR-39), measuring 1.2 mm in thickness, 300 mm in outer diameter, and 35 mm in inner diameter, was fixed in a chamber of a vacuum vapor deposition device equipped with three electron guns. In four crucibles, Ge, Sn, Au and SnO<sub>2</sub> were loaded, respectively. While said base plate was driven to rotate at 20 rpm, with a vacuum degree of 1 x  $10^{-6}$  mm Hg, a Ge layer with thickness of 50 Å was first vapor deposited; then, Sn, Au and SnO<sub>2</sub> were irradiated with separate electron guns and Sn, Au, and SnO<sub>2</sub> were evaporated at different evaporating rates, respectively, to perform simultaneous vapor deposition of the three components so as to form a composite layer with thickness of 150 Å and having Sn-Au alloy fine grains, composed of 90 wt% of Sn and 10 wt% of Au in SnO<sub>2</sub>, dispersed in the SnO<sub>2</sub> with the filling rate of the fine alloy grains of 0.7. Then, on the composite layer, a Ge layer of 50 Å was vapor deposited. As a result, a disk-shaped optical recording medium having a recording layer of 250 Å having a configuration with n = 2 in Figure 2 was formed.

For the optical recording medium obtained, the recording/reproduction characteristics were measured using the same method as that in Application Example 1, with results listed as sample No. 3-1 in Table 3.

Also, optical recording media sample Nos. 3-2 to 3-6 listed in Table 3 were prepared using the same method as said sample No. 3-1, with the same type of base plate, the same type and thickness of the semiconductor layer, the same filling rate of the fine alloy grains in the composite layer, the same thickness of the composite layer, the same constitution of the recording layer, and the same thickness of the recording layer as those in sample No. 3-1, except that the type and composition of the alloy in the composite layer are listed in Table 3. For the optical recording media with sample Nos. 3-2 to 3-6, measurement was performed under the same conditions as in Application Example 1, with the obtained recording/reproduction characteristics listed in Table 3.

The stability and moisture resistance were measured in the same way as in Application Example 1, and they were found to be good.

EX 1 15 F3	協会関中の合金数数子の 機関と組成性	化的异生物性		
	(REM)	レーザ光鉄度 (xii)	CNH (db)	
3-1	Sn (90) 44 (10)	7	5 S	
3 - 2	So (20) Au (80)	9	\$ \$	
3 ~ 3	Sa (95) -4, (4)	8	5.5	
3 ~ 4	in 1907) ,Pb ((0)	7	5 3	
. 3 ~ 5	Sa (50) In (50)	7	5.4	
3 - 6	(a (80) -\$a (20)	7	5 6	

Table 3.

- Key: 1 Sample No.
  - 2 Type and composition of fine alloy grains in composite layer
  - 3 Recording/reproduction characteristics
  - 4 Laser beam intensity (mW)
  - 5 CN ratio

## Brief description of the figures

Figures 1, 2, 3, 4 and 5 are cross-sectional views illustrating the optical recording media of the present invention.

- l Composite layer
- 2 Semiconductor layer
- 3 Base plate



Figure 1



Figure 2



Figure 3



Figure 4



Figure 5